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ON A SYSTEMATIC ERROR IN THE X-RAY DETERMINATION OF THE IRON CONTENT OF CHLORITES AND BIOTITES

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Brindley and Gillery (1956) proposed a method for the X-ray determination of the iron content in chlorites; the foundation of the method is measurement of intensity of some basal reflections.

Gottardi (1957) in applying this method found a value 17 percent larger than that given by chemical analysis. Gower (1957) and Franzini Schiaffino (1965) proposed X-ray methods for determination of iron content in biotites, which also required measurement of the reflection intensity of basal planes. Hörmann and Morteani (1966) in applying the latter methods have found values from 0 to 20 percent higher than chemical analysis.

These errors are much higher than the probable errors given by the authors who proposed the methods, and also higher than would be suggested by an informed guess. Only positive errors are mentioned.

A possible explanation of these systematic errors is given here. The proposers' methods of determination were worked out with pure and homogeneous samples. The authors tried to apply the methods to samples of rock minerals, and probably in both cases the samples were composed of many crystals, in which the ratio Fe/Mg was variable and had a Gaussian scatter around an average value (it does not matter if the scatter was not truly gaussian). Now let us suppose, that such a scatter of the ratio Fe/Mg really existed in the samples of Gottardi (1957) and of Hörmann and Morteani (1966), and these contained a "population" of crystals. In order to simplify the matter, let us divide each population into two fractions, the first (called "ferrous") containing all crystals with an iron content higher than the average for the population, the second (called "magnesian") containing all crystals with an iron content lower than the average for the population. Now it is obvious that in X-ray powder patterns (orientated or not) the "ferrous" fraction contributes more to each diffraction peak than the "magnesian" fraction, for two reasons:

1. The crystals of the "ferrous" fraction have higher structure factors than the crystals of the "magnesian" fraction (this holds for all relevant diffractions taken into account in the mentioned papers; some reflections are not affected by the iron content, as they are considered only as internal standards), so the "ferrous" crystals have more weight in the average structure factor than "magnesian"

crystals. What we really need is the average value of the structure factors; what we in fact measure is an average intensity value (proportional to the square of the structure factors). As the square root of the average of the squares of a set of different values is always larger than the average of the same set, the average structure factor deduced from an observed intensity for a population of crystals is always larger than the average structure factor of the population, and the iron content deduced is thus too high. This error does not affect the method of Franzini and Schiaffino (1965) and part of the method of Gower (1957), as they are based on intensities rather than on structure factors.

2. "Ferrous" crystals are more X-ray absorbent than "magnesian" crystals, so, if in an orientated aggregate two crystals of the two different fractions are superimposed, and if the "magnesian" crystal is on top of the "ferrous" crystal, both contribute to the diffraction; if, on the contrary, the "ferrous" crystal is on top, only the "ferrous" crystal contributes to the diffraction (a rather simplified explanation of the phenomenon). Brindley and Gillery (1956, in the Appendix, under the title *Other Difficulties*) write something analogous when describing the "other difficulties inherent in the precise interpretation of X-ray intensities"; they write: "When composite specimens containing several crystalline components are used, questions of differential absorption arise particularly when absorption coefficients of the components are very different." But I think this sentence emphasizes the possibility of an error in intensity measurements arising when a sample is composed of a chlorite mixed with another mineral with different absorption power, rather than when a sample is composed of many chlorite crystals with similar, but different chemical composition.

So it is quite evident that, if the two mentioned methods are applied to samples composed of crystals whose chemical composition is scattered at random around an average value, the result will always be a high iron content. This systematic error towards higher iron contents is proportional to the degree of scatter of the chemical composition of the different crystals (and the error is zero when all the crystals have exactly the same chemical composition).

It must also be pointed out that in the determinative methods, which require the measuring of spacings in powder diagrams, an analogous error is possible, even though less striking.

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CHANGES IN K-FELDSPAR STAINING METHODS  
AND ADAPTATIONS FOR FIELD USE

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This note describes changes found useful in staining methods for differentiation of K-feldspar and plagioclase, and adaptations of the changes for use in the field. The method used is the hydrofluoric acid etch and staining of K-feldspar with sodium cobaltinitrite.

Staining of K-feldspar with sodium cobaltinitrite was proposed by Gabriel and Cox (1929), and further developed by Keith (1939), Chayes (1952), Jackson and Ross (1956), Rosenblum (1956), and Bailey and Stevens (1960).

It has been found that etching hand specimens and rock slabs by submerging a portion of them in concentrated hydrofluoric acid gives good K-feldspar staining on all rock samples (granitic to dioritic igneous rocks and many types of gneisses and schists). The rock is put into the acid for 15-20 seconds, dipped into water to remove the acid, and while still wet, put into the saturated sodium cobaltinitrite solution for 1-2 minutes. After the specimen is rinsed in tap water and allowed to dry, the K-feldspar is stained bright yellow, the plagioclase is chalky white, and the quartz is a dull gray. The advantages of this method are that it allows many specimens to be stained in a short time and that a close visual estimation of the amounts of K-feldspar and plagioclase may be obtained by staining only the K-feldspar.

The method has been adapted to field use with a small plastic squeeze bottle of hydrofluoric acid and a dropper bottle of sodium cobaltinitrite solution. Several drops of acid are applied to the surface of the hand specimen and spread with the tip of the bottle. After 15-20 seconds, the specimen is rinsed with any handy supply of water, the sodium cobaltinitrite is applied, and after one minute, again rinsed. K-feldspar, plagioclase, and quartz may be differentiated as explained above.

Information gained by using staining in the field has been found to be